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GAINS AND LOSSES OF MINERAL ELEMENTS IN AN IRRIGATED SOIL DURING A 20-YEAR LYSIMETER INVESTIGATION¹

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INTRODUCTION

THE MAIN OBJECTIVE in the investigation reported herein was to determine N gains and losses with various combinations of winter crops and fertilizer applications. A secondary objective was to determine the gains and losses of Ca, Mg, Na, K, Cl, S and P. Seven of these elements are essential for the growth of plants and the element Na, although not essential for plants, is of interest as one of the detrimental components in salt-affected soils.

Chapman, Liebig and Rayner (1949)⁴ reported the N gains and losses during the first 10 years and Broadbent and Chapman (1950) reported data summarizing the first 15 years of the experiment. The purpose of this report is to present data for the complete experiment. Although some of the conclusions are the same as previously reported, the data for the last five years and a more complete analysis of the soil at the end of the experiment have added considerably to the value of the experiment. Enough new relationships and conclusions have emerged to justify an additional publication.

DESCRIPTION OF THE EXPERIMENT

Tanks and Soil. The tanks were made of 16-gauge galvanized iron. They were 10 feet in diameter and 4 feet deep with funnel-shaped bottoms. The tanks were filled with soil in 1926. An 8-inch layer of No. 3 flint rock, ranging in size from $\frac{3}{8}$ to $1\frac{1}{2}$ inches in diameter, was placed in the bottom to provide a filter for the soil. The soil was taken from the surface foot of a virgin granitic-derived residual soil formerly classified as a Sierra loam

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⁴ See "Literature Cited" for citations referred to in text by author and date.

but now classified as a Holland loam. From 1926 to 1933 the soil was unirrigated and clean cultivated so that vegetation was not allowed to grow. Soil samples were taken in 1933 and the experiment was started with a crop of barley in all tanks in the summer of 1934. Additional soil samples were taken in 1939, 1944, 1949, 1954.

Treatments. The treatments consisted of the application of cereal straw and the growth of vetch, melilotus and mustard covercrops, each in combination with 0, 100, and 200 pounds N per acre per year from $\text{Ca}(\text{NO}_3)_2$. Thus, there were twelve treatments and no true replication. The value of the experiment would have been increased by adding replicates. However, there was more than ample replication in years and there was replication in the sense that each N rate was applied to each of four crops or crop residue treatments.

The treatments described above were winter treatments. The $\text{Ca}(\text{NO}_3)_2$ was added to the winter crop and was applied at time of planting for the 100 pound rate, but for the 200 pound rate half was added at planting time and half was added at the time the covercrops were worked into the soil. The $\text{Ca}(\text{NO}_3)_2$ added with the straw was applied when the straw was spaded into the soil; straw was added at a rate of 500 pounds per acre per year. The summer crop which was grown uniformly in all tanks was barley from 1934 to 1939 inclusive and Sudangrass from 1940 to 1953 inclusive. The total of the aboveground portion of the plants of all crops was removed, weighed, and samples taken for analysis. The winter crops were returned to the soil but the summer crops were not returned and thus the summer crop was used to deplete the soil.

Irrigation Water. The irrigation water was fairly constant in composition during the 20 years of the experiment. The average mineral content was 2.43 me. Ca, 1.46 me. Na, 0.76 me. Mg, 0.63 me. Cl, 1.03 me. SO_4 , and 3.00 me. HCO_3^- per liter. The water was of good quality with a conductivity of 0.570 millimhos per cm. and a Na content of 31 per cent. The water contains no residual Na_2CO_3 , but assuming that all of the HCO_3^- was precipitated by Ca and Mg, the Na content of the water would be 88 per cent.

Irrigation water was added in sufficient quantities to supply the needs of the crops. Leaching resulted from the application of irrigation water only once during the experiment. This occurred in the spring of 1939 when extra water was added to promote leaching and the removal of accumulated nitrates.

Rainfall. The average rainfall for the 20 years was 9.26 inches per year with annual variations from 5.45 to 22.47 inches. The rainfall came mostly in the winter months. During 10 of the 20 years leaching resulted from rainfall.

The average N content of the rain was 1.1 pounds per acre per year with variations from 0.2 to 2.3. The Cl and S contents of the rain of the 1953-54 season were 3.2 and 4.9 pounds per acre respectively. The total rainfall during the 1953-54 year was 9.14 inches.

RESULTS

Yield and Nitrogen Content of Crops. Data for the average yield of dry matter of crops are presented in table 1. There were small but consistent increases in yield of the annual legumes as a result of N applications. These increases in yields were certainly not economical and in no way justify the application of N to such crops. However, they do indicate that at some time in the growth of these crops N fixation by the legume nodule bacteria present was not sufficient to give maximum growth rate.

There were large increases in yield of mustard with increases in N fer-

TABLE 1

AVERAGE YIELD OF DRY MATTER OF WINTER CROPS FOR FOUR 5-YEAR PERIODS AND FOR WINTER AND SUMMER CROPS FOR THE TOTAL EXPERIMENT

Crop	Fertilizer $\text{Ca}(\text{NO}_3)_2$	Winter crops					Summer crop* 1934-1954
		1934-1939	1939-1944	1944-1949	1949-1954	1934-1954	
	lbs N/A	lbs/A	lbs/A	lbs/A	lbs/A	lbs/A	lbs/A
Straw.....	none	7220
Straw.....	100	9170
Straw.....	200	8810
Mustard.....	none	3540	990	318	1220	1520	6820
Mustard.....	100	4630	4240	3220	5000	4270	8700
Mustard.....	200	4720	5330	4040	5830	4980	8630
Vetch.....	none	5420	4220	5880	5170	5170	8120
Vetch.....	100	5530	4640	6500	5750	5610	8120
Vetch.....	200	5690	4750	6760	5790	5750	8360
Melilotus.....	none	4630	3670	4470	3790	4140	8620
Melilotus.....	100	4500	4570	5230	4720	4750	8530
Melilotus.....	200	4720	4420	5500	5000	4900	8640

* Summer crop was the same for all treatments.

tizer except in the first five years when the soil contained a large amount of nitrate N accumulated from the 1926-34 fallow period.

The yield of the summer crop was increased by about a ton per year by applications of N where the winter treatment was mustard or straw. The N needed to produce these large yields of the summer crop, where no N was added, came mainly from decomposition of soil organic matter in the turned under mustard and straw. Temperature and moisture conditions were favorable during the summer for rapid mineralization of organic matter whereas in winter during the growth of the mustard crop the temperature was low enough that mineralization was extremely slow.

Where the winter crop was a legume there were no increases in yield of the summer crop as a result of N fertilization. Enough N was fixed by the legumes to fully meet the N requirements of the summer crop.

The relation between the average N in tops of plants of winter crops and the annual rate of application of N to the soils as $\text{Ca}(\text{NO}_3)_2$ for the last 15

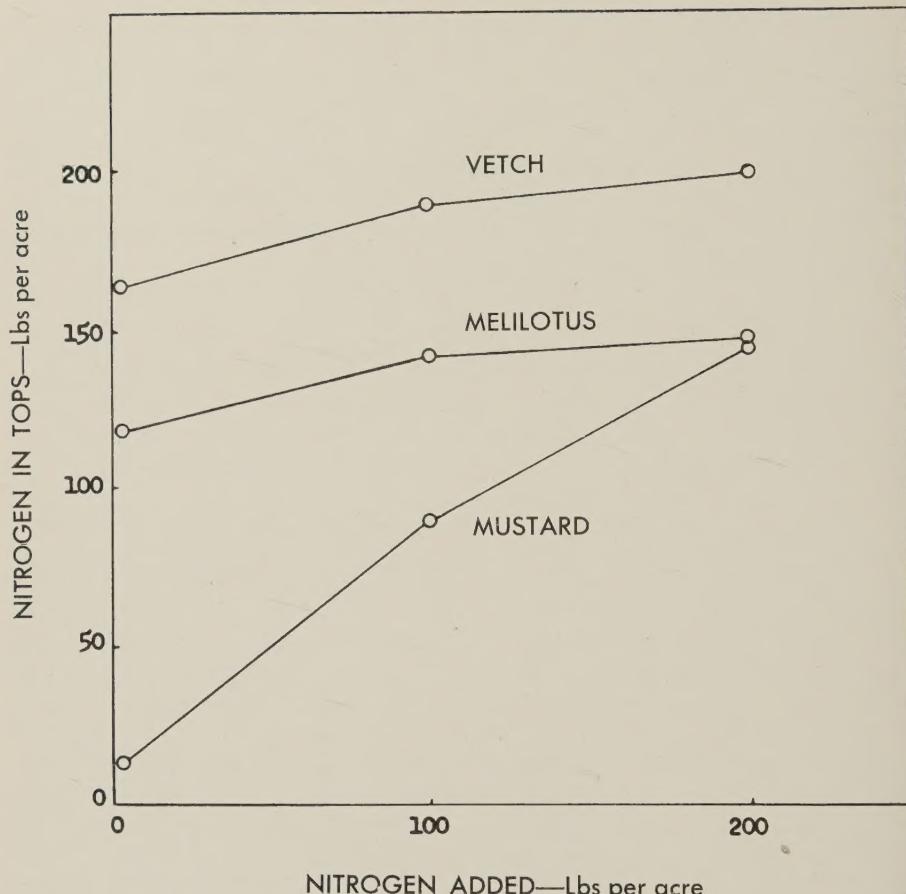


Fig. 1. Relation between average N in tops of plants in last 15 years of the experiment and the annual rate of application of N as $\text{Ca}(\text{NO}_3)_2$.

years of the experiment is presented in figure 1. The first 5 years' data were not used in this case because of the high nitrate-N content of the soil during that period. The N in the mustard crop with no N added was about 12 pounds per acre per year. This is not much greater than the N in the rain plus that in the irrigation water. Thus, practically no N was released from the soil during the growth of this crop. When N was added to the soil the apparent recovery by mustard was about 80 per cent at the 100-pound rate and about 70 per cent at the 200-pound rate.

Both of the legume crops showed increased N in tops with increased amounts of N added to the soil. Using calculated N fixation data (see section on *Nitrogen Gains and Losses*) to correct for contributions from the nodule bacteria the apparent N recovery by the vetch was 52 and 90 pounds per acre per year or 52 and 45 per cent for N at the 100- and 200-pound rate respectively. Corresponding data for melilotus were 72 and 47 per cent recovery.

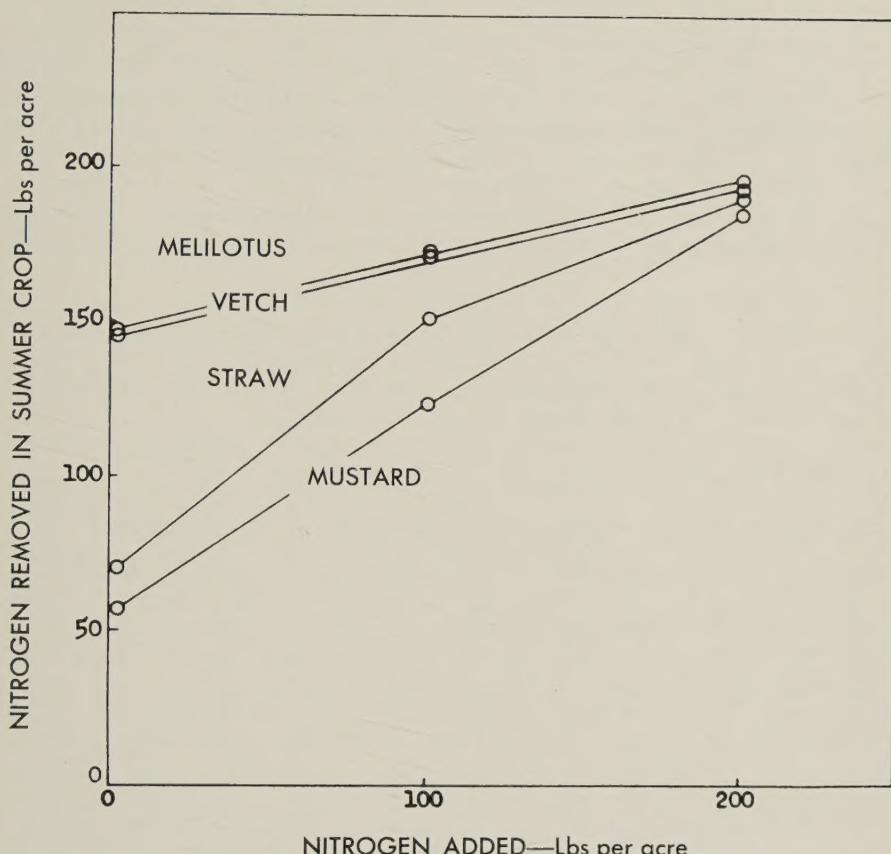


Fig. 2. Relation between average N removed in summer crop during last 15 years of the experiment and the annual rate of application of N as $\text{Ca}(\text{NO}_3)_2$.

Figure 2 presents the relation between the average N removed in the summer crop and the annual rate of application of N as $\text{Ca}(\text{NO}_3)_2$. Although the rate of application of $\text{Ca}(\text{NO}_3)_2$ had only a small effect on yields of the summer crop it had a large effect on N removal, particularly with the straw and mustard winter treatments. Yield increases were only about 25 per cent whereas increases in N removal were increased about threefold.

Vetch and melilotus without N were 75 per cent as effective as mustard with the highest rate of N in supplying N to the summer crop. Comparing the legumes with mustard the legumes alone were equivalent to mustard plus 135 pounds of N from fertilizer. This agrees well with N fixation data of 131 and 124 pounds N per acre per year for vetch and melilotus respectively.

Nitrogen. Data on the gains and losses of N in soil for four 5-year periods and for the total period of the lysimeter experiment, and the total gains and losses as a percentage of the total N in the soil at the beginning of the experiment are presented in table 2. These data represent the sum of the

additions from seed, rain, irrigation water, fertilizer, and straw, plus release from the soil subtracted from the sum of the removals in crops and leachate. The difference, if positive, represents an increase in N and is assumed to be a fixation from atmospheric N; if negative, it is assumed to be a volatilization loss of added N. The contribution from the soil was calculated from a determination of total N of soil samples taken in June of 1933, 1939, 1944, 1949, and 1954.

The data for the vetch and melilotus cover crops are positive and thus indicate a fixation of N by these crops. Total fixation in the 20-year period

TABLE 2

GAINS AND LOSSES OF N IN SOILS FOR FOUR 5-YEAR PERIODS AND FOR THE TOTAL PERIOD OF A LYSIMETER EXPERIMENT, AND TOTAL GAINS AND LOSSES AS PERCENTAGES OF TOTAL N IN THE SOIL AT THE BEGINNING OF THE EXPERIMENT

Treatment		Nitrogen gains or losses in soil*					Total gain or loss N in soil
		1934-1939	1939-1944	1944-1949	1949-1954	Total	
Crop material or covercrop	Calcium Nitrate	lbs/A	lbs/A	lbs/A	lbs/A	lbs/A	Total gain or loss N in soil
	lbs N/A	lbs/A	lbs/A	lbs/A	lbs/A	lbs/A	
Cereal straw.....	0	-128	240	83	-112	83	1.2
Cereal straw.....	100	-171	131	-141	212	31	0.4
Cereal straw.....	200	-261	-189	-36	350	-136	-1.9
Mustard covercrop	0	-228	199	82	-227	-174	-2.5
Mustard covercrop	100	-319	226	-49	234	92	1.3
Mustard covercrop	200	-206	-317	-24	244	-303	-4.3
Vetch covercrop	0	315	741	835	738	2629	37.6
Vetch covercrop	100	345	684	115	971	2115	30.8
Vetch covercrop	200	248	429	535	327	1539	22.0
Melilotus covercrop	0	348	833	825	466	2472	35.4
Melilotus covercrop	100	115	386	410	737	1648	23.5
Melilotus covercrop	200	224	150	728	243	1345	19.2

* Nitrogen fixation if positive and volatilization if negative.

averaged 131, 106, and 77 pounds per acre per year, respectively, for vetch at 0, 100, and 200 pounds N per acre per year. Total fixation by melilotus averaged 124, 82, and 67 pounds per acre per year, respectively for the same rates of N applications. These data are sufficiently large and so consistently positive that there should be no question about their significance.

Variations in N fixation by legumes in the four 5-year periods are relatively large. These variations are not associated with yields or with any environmental or soil factors that were measured but appear to be random with no interaction between periods and N fixation.

The data for the total experiment suggest no significant gains or losses of N for either the straw or the mustard covercrop treatments. The largest positive value of the total N in the soil at the beginning of the experiment is 1.3 per cent, and the largest negative value is 4.3 per cent. In contrast, the smallest value for N fixation with legumes was 19.2 per cent of the total

N in the soil. Thus, on the average, with straw or mustard there was neither a net fixation nor a net volatilization of nitrogen during the 20 years of the experiment. There were variations among the data for the four 5-year periods but these variations appeared to be random and not associated or correlated with periods or with the environmental factors that were measured.

Since the increase or decrease in total soil N enters into all the calculations of gains or losses of N, one must consider the gains or losses of N in relation to the errors involved in measuring the total soil N in the tanks. The original total soil N was about 7,000 pound per acre. Chapman, Liebig and Rayner (1949), in discussing the first 10 years of the experiment, estimated that differences of greater than 150 to 200 pounds N per acre from one sampling period to the next would be real. Broadbent and Chapman (1950), however, found that variations in the 1949 soil samples were such that values as great as 320 pounds per acre might not be significant at the 5 per cent level of probability. The 320 pounds N per acre represent 4.6 per cent of the original N content of the soil. The values for total N gains or losses with the mustard and cereal straw treatments are less than this value and are thus likely to be non-significant.

In this experiment there was no evidence of reducing conditions in the soils. Drainage water was always free of reduced forms of Fe and Mn. (Data obtained recently from filled-in lysimeters containing 5.5 feet of soil show that when reducing conditions are attained the drainage water may contain as much as 12 ppm. Mn and 8 ppm. Fe, and that when exposed to the air, these elements are oxidized and precipitated as oxides.) Thus the absence of volatilization losses of N can be attributed to lack of reducing conditions in the soil. However, there is also the possibility that losses did take place and that these were balanced by nonsymbiotic N fixation.

If the N gains and losses with the non-legume treatments, expressed as percentages of the total N in the soil, are used as estimates of experimental error, they indicate that the experiment was well conducted, that no gross errors were involved, and that all samples of water, soil, plants, and leachate were representative of the totals of these materials in the experiment.

The data show that relatively large amounts of N can be fixed by annual winter legume crops and that the maximum fixation is obtained when the soil contains a low supply of available N. The N fixation is also dependent on the growth of the legume crop. In the lysimeters the dry weight yields were relatively large and thus conditions were extremely favorable for N fixation.

One might expect similar quantities of fixation in the field only if similar favorable conditions are found. Where shading, drought, salinity, nutrient deficiencies or other soil or environmental factors limit yields, or where the soil is supplied with available N, the fixation may be reduced to a small fraction of the values reported here.

The data for the cereal straw treatments and the mustard covercrop suggest that volatilization losses of N are not serious where care is taken to avoid waterlogging the soil and that the usual irrigation practices on soils that are internally well drained do not produce volatilization. Thus, the usual mechanism of N depletion are crop removal and leaching losses. It is well

established, however, that volatilization does take place when reducing conditions are established by prolonged saturation of the soil with water.

The foregoing statements apply to neutral and alkaline soils fertilized with $\text{Ca}(\text{NO}_3)_2$. There is evidence from other sources that there can be N volatilization losses from acid or alkaline soils fertilized with urea and ammonium sources of N under normal aerobic conditions. Allison (1955) in a review of the literature dealing with N gains and losses in lysimeters and in field trials reported that most experiments show an unaccounted-for loss of N which is assumed to be loss by volatilization. The absence of loss

TABLE 3
POTASSIUM ADDED AND REMOVED AND DEPLETION FROM THE
SOILS DURING 20 YEARS

Treatment		Potassium added*	Potassium removed			Depletion of soil
Winter crop	$\text{Ca}(\text{NO}_3)_2$		Crop	Leaching	Total	
	$\text{lbs } \text{N/A}$	lbs/A	lbs/A	lbs/A	lbs/A	lbs/A
Straw.....	none	1721	3418	20	3438	1717
Straw.....	100	1726	4376	33	4409	2683
Straw.....	200	1725	4701	50	4751	3026
Mustard.....	none	198	3208	23	3231	3033
Mustard.....	100	235	4483	25	4508	4273
Mustard.....	200	237	4853	16	4869	4632
Vetch.....	none	239	3880	15	3895	3656
Vetch.....	100	245	4021	22	4043	3798
Vetch.....	200	247	4476	25	4501	4254
Melilotus.....	none	230	4013	31	4044	3814
Melilotus.....	100	232	4382	34	4422	4190
Melilotus.....	200	234	4581	36	4617	4383
Average.....		606	4199	28	4227	3621

* Potassium added in water except for 1574 lb. K per acre added in straw.

of N in this experiment might be attributed to the alkaline conditions of the soil combined with a nitrate source of N.

Phosphorus. There was little if any P added in irrigation water or in fertilizer or straw. Also, the drainage water had little if any P. Thus the P removed by cropping represented depletion. The average removed by crops was 317 pounds per acre for the 20-year period, or 15.9 pounds per acre per year.

Potassium. Data for the K added and removed and depletion from the soil are presented in table 3. The average depletion was 181 pounds K per acre per year mostly by crop removal. Very little K was lost by leaching and only a relatively small amount was added in the irrigation water.

Magnesium. Data for gains and losses of Mg are presented in table 4. The Mg added was mostly added in the irrigation water. Removal was about equally distributed between crop removal and leaching. Within each winter crop or crop residue treatment there was a decrease in Mg accumulation or an increase in Mg loss with increase in rate of application of $\text{Ca}(\text{NO}_3)_2$.

TABLE 4
GAINS AND LOSSES OF MAGNESIUM DURING THE 20 YEARS OF THE
LYSIMETER EXPERIMENT

Treatment		Ca(NO ₃) ₂	Magnesium added*	Magnesium removed			Added minus removal
				Crop	Leaching	Total	
Winter crop		lbs/A	lbs/A	lbs/A	lbs/A	lbs/A	lbs/A
Straw.....	none	780	307	508	815		-35
Straw.....	100	812	518	576	1094		-282
Straw.....	200	808	582	750	1332		-524
Mustard.....	none	938	325	428	753		185
Mustard.....	100	1080	546	394	940		140
Mustard.....	200	1100	634	383	1017		83
Vetch.....	none	1100	597	196	793		307
Vetch.....	100	1120	581	516	1097		23
Vetch.....	200	1120	646	582	1228		-108
Melilotus.....	none	1060	594	412	1006		54
Melilotus.....	100	1060	624	491	1115		-55
Melilotus.....	200	1070	647	635	1282		-212
Average.....		1004	550	489	1039		-35

* Magnesium in the irrigation water except 90 lbs/A added in straw.

TABLE 5

SODIUM ADDED, REMOVED BY CROPPING AND LEACHING, ACCUMULATION
IN THE SOIL AND REMOVAL AS A PERCENTAGE OF TOTAL ADDED

Treatment		Sodium added*	Sodium removed			Sodium added minus removed	Percentage removal		
Winter crop	Ca(NO ₃) ₂		Crop	Leaching	Total		Totals	Crop	Leaching
		lbs N/A	lbs/A	lbs/A	lbs/A	lbs/A			
Straw.....	none	2540	166	680	846	1694	33	7	26
Straw.....	100	2640	253	723	976	1664	37	10	27
Straw.....	200	2630	263	771	1034	1596	39	10	29
Mustard.....	none	3240	240	1180	1420	1820	44	8	36
Mustard.....	100	3770	305	927	1232	2538	33	8	25
Mustard.....	200	3810	352	607	959	2851	25	9	16
Vetch.....	none	3320	285	503	788	2532	24	9	15
Vetch.....	100	3880	302	656	958	2922	25	8	17
Vetch.....	200	3800	337	627	964	2836	25	9	16
Melilotus.....	none	3670	290	985	1275	2395	35	8	27
Melilotus.....	100	3690	300	832	1132	2558	31	8	23
Melilotus.....	200	3720	349	853	1202	2518	32	9	23
Average.....		3390	287	778	1065	2325	31	9	23

* Sodium added was in the irrigation water except for 135 lbs/A added in the straw.

TABLE 6
GAINS AND LOSSES OF Cl AND PERCENTAGE REMOVAL OF ADDED
Cl by CROPS AND BY LEACHING

Treatment		Chloride added*	Chloride removed			Added minus removed	Percentage removal	
			Crop	Leaching	Total		Crop	Leaching
Winter crop	Ca(NO ₃) ₂	lbs/A	lbs/A	lbs/A	lbs/A	lbs/A	per cent	per cent
Straw.....	none	2136	1607	675	2282	-146	75	32
Straw.....	100	2205	1726	501	2227	-22	78	23
Straw.....	200	2198	1743	457	2200	-2	79	21
Mustard.....	none	2025	1472	557	2029	-4	73	27
Mustard.....	100	2328	1990	277	2267	61	85	12
Mustard.....	200	2372	2036	215	2251	121	86	9
Vetch.....	none	2389	1933	162	2095	294	81	7
Vetch.....	100	2431	1846	336	2182	249	76	14
Vetch.....	200	2428	1894	258	2152	276	78	11
Melilotus.....	none	2300	1987	422	2409	-109	86	18
Melilotus.....	100	2308	1962	366	2328	-20	85	16
Melilotus.....	200	2332	1912	452	2364	-32	82	19
Average.....		2288	1842	390	2232	56	81	17

* Chloride added was from the irrigation water except for 629 lbs/A added in straw.

TABLE 7
GAINS, LOSSES, AND ACCUMULATION OF CALCIUM IN LYSIMETERS
DURING 20 YEARS OF TREATMENT AND THE CaCO₃ DETERMINED
IN THE SOIL AFTER THE 20-YEAR PERIOD

Winter treatment		CaCO ₃ equivalent of Ca, lbs. per acre								
		Ca(NO ₃) ₂ lbs. N per acre	Crop or crop material*	Irrigation water	Fertilizer and straw	Total added	Removal in summer crop	Removal in leachate	Total removal	Added minus removal
0	Cereal straw....	8,960	740	9,700	2,130	4,620	6,750	2,950	4,030	
0	Vetch.....	14,260	0	14,260	2,760	2,910	5,670	8,590	7,500	
0	Melilotus.....	13,760	0	13,760	2,880	3,860	6,740	7,020	7,200	
0	Mustard.....	12,140	0	12,140	1,980	4,040	6,020	6,120	5,710	
100	Cereal straw....	9,360	7,520	16,860	2,920	5,400	8,320	8,540	8,250	
100	Vetch.....	14,520	6,780	21,300	2,910	4,730	7,640	13,660	12,600	
100	Melilotus.....	13,780	6,780	20,560	2,940	4,330	7,270	13,290	11,100	
100	Mustard.....	14,070	6,780	20,850	2,790	3,690	6,480	14,370	15,450	
200	Cereal straw....	9,300	14,300	23,600	3,130	7,370	10,500	13,100	8,400	
200	Vetch.....	14,560	13,560	28,120	3,330	5,430	8,760	19,360	13,800	
200	Melilotus.....	13,900	13,560	27,460	3,220	5,830	9,050	18,410	13,200	
200	Mustard.....	14,200	13,560	27,760	3,130	3,570	6,710	21,050	19,400	
	Average.....			19,700	2,840	4,650	7,490	12,200	10,550	

* Winter crops were not removed from tanks.

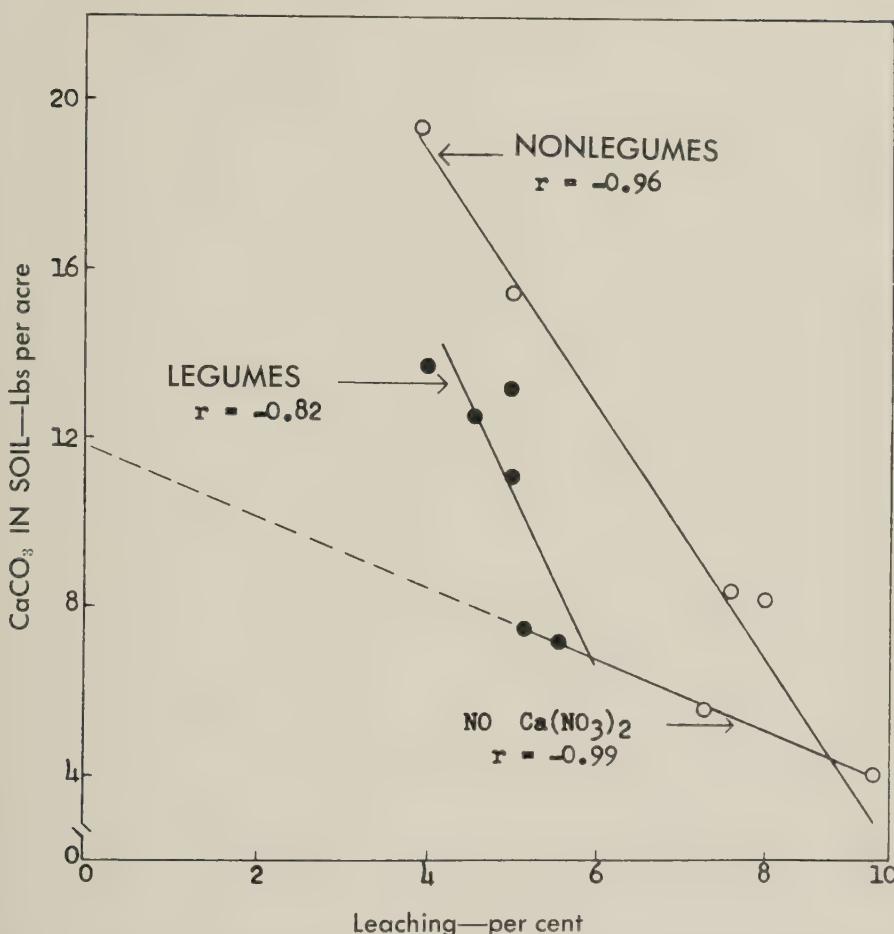


Fig. 3. Relations between CaCO₃ accumulation in the soil and leaching as a per cent of total irrigation water added for non-legumes, legumes and no Ca(NO₃)₂ treatments.

This relationship between Mg loss from the soil and amount of salts added as fertilizer is the same as reported by Pratt and Harding (1957) for the soil of a long-term fertility trial.

The losses of Mg by leaching were increased by increases in Ca(NO₃)₂ except in the case of the mustard winter crop, where the Ca(NO₃)₂ applications, because of increased growth of the crop, reduced the amount of leachate from 7.3 per cent with no N applied to 3.9 per cent with 100 pounds N per acre. In all cases there were increases in Mg removal by cropping with increases in Ca(NO₃)₂. This effect was greatest with the straw and mustard winter treatments.

Sodium. Data for Na added, removed by cropping and leaching, accumulation in the soil, and that removed as a percentage of the total added, are

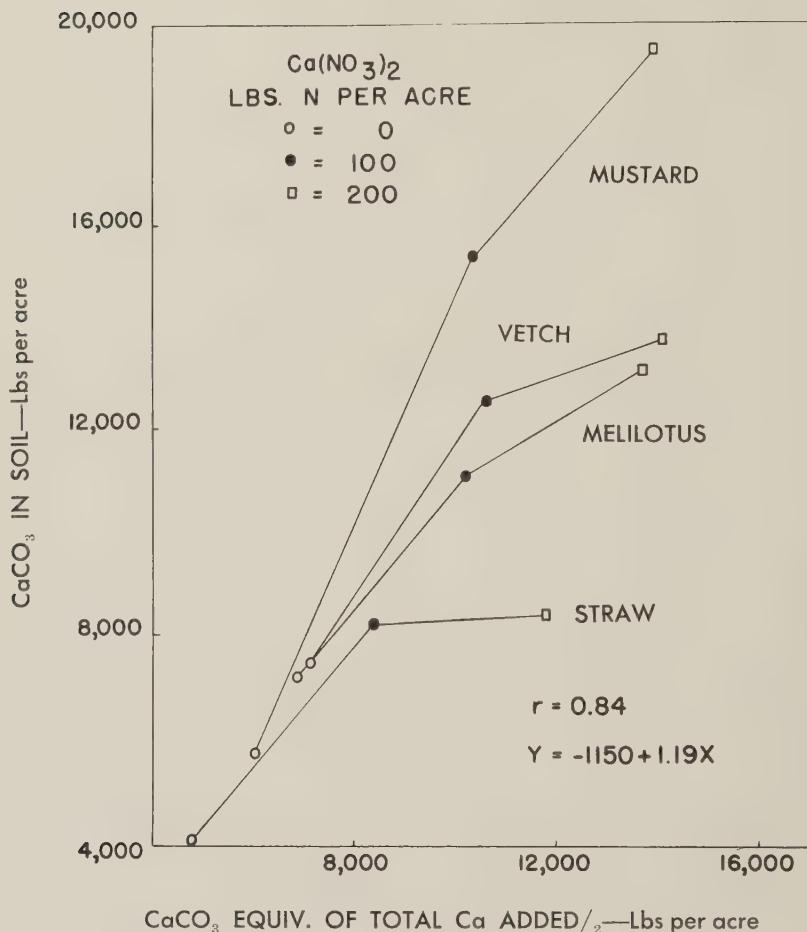


Fig. 4. Relationship between CaCO₃ in the soil and the CaCO₃ equivalent of half the total Ca added to the lysimeters in 20 years.

presented in table 5. The Na accumulation averaged 69 per cent of that added.

About 85 per cent of the Na removed by crops was removed by the six crops of barley. If barley had been continued as the summer crop the removal of Na would have been about 55 per cent of the total added.

Chloride. Data for the gains and losses of Cl and the percentage removal of added Cl by crops and by leaching are presented in table 6. Both barley and Sudan grass removed relatively large quantities of Cl and as a result the major portion of the Cl removed was removed by the summer crops. The average accumulation was only 2 per cent of that added.

Sulfur. The average S added to the tanks in 20 years was 1,700 pounds per acre. Of this 290 pounds was removed by crops, 1,070 pounds was removed by leaching and 337 pounds accumulated in the soil. The range of values for accumulation was from 898 to a -128 pounds per acre. The aver-

age S accumulation per acre per year was 16.8 pounds, which is not a large yearly accumulation considering the fact that crop removal was small and leaching occurred during only half of the 20 years of the experiment.

Calcium. Data for gains, losses and accumulation of Ca during the experiment and the CaCO_3 determined in the soil at the end of the experiment are presented in table 7. For all treatments over the 20-year period the average Ca added minus the average removed was 12,300 pounds CaCO_3 equivalent per acre. The average CaCO_3 in the soil at the end of the ex-

TABLE 8

THE CaCO_3 EQUIVALENT OF THE HCO_3^- ADDED IN THE IRRIGATION AND THE CaCO_3 IN THE SOIL AS A PER CENT OF THE HCO_3^- ADDED

$\text{Ca}(\text{NO}_3)_2$ lbs/acre	Winter treatment		CaCO_3 equivalent of HCO_3^- added in irrigation water* lbs/A	CaCO_3 in soil as per cent of HCO_3^- added
	Crop or crop material			
0	Straw.....		11,050	36.5
	Vetch.....		17,600	42.6
	Melilotus.....		17,000	42.3
	Mustard.....		15,000	38.1
	Average.....			39.9
100	Straw.....		11,550	71.4
	Vetch.....		17,950	70.2
	Melilotus.....		17,030	65.2
	Mustard.....		17,400	89.0
	Average.....			74.0
200	Straw.....		11,500	73.2
	Vetch.....		17,650	78.2
	Melilotus.....		17,200	76.8
	Mustard.....		17,510	111.0
	Average.....			84.8

* Assuming the reaction is $\text{Ca}^{++} + 2\text{HCO}_3^- = \text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2$.

periment was 10,550 pounds per acre, which is 86 per cent of the Ca that accumulated in the soil. The other 14 per cent was probably used to bring the pH of the soil from slightly acid to values between 7.8 and 8.3. The correlation coefficient for the relationship between Ca accumulation and Ca determined as CaCO_3 in the soil was +0.92, thus indicating that the CaCO_3 precipitation was highly associated with, and most likely a function of, the Ca accumulation.

The relations between CaCO_3 accumulation in the soil and leaching percentage for the non-legume, legume and no $\text{Ca}(\text{NO}_3)_2$ treated tanks are presented in figure 3. The mustard winter crop produced a greater CaCO_3 precipitation than the legume crops at the same leaching percentage. The cause of the difference is not apparent but might have been caused by a greater drying of the soil during the autumn when the winter crops were becoming established. The mustard, particularly when fertilized with

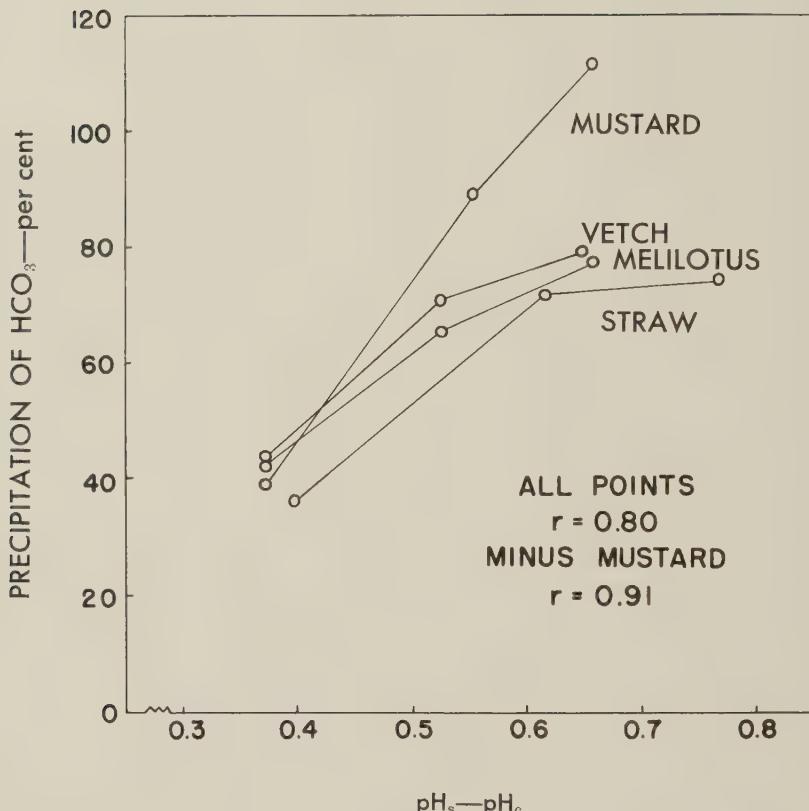


Fig. 5. Relation between per cent precipitation of the HCO_3^- added in irrigation water and the difference between the measured pH of the paste and the pH that would be found in an equilibrium solution with CaCO_3 at the HCO_3^- and adjusted Ca content of the irrigation water.

$\text{Ca}(\text{NO}_3)_2$ grew much faster in the early season than the slow-starting legumes.

The Y-intercept value for the regression for the four tanks that received no $\text{Ca}(\text{NO}_3)_2$ is 11,900 pounds CaCO_3 per acre, which is only 600 pounds less than the average Ca added to these tanks. The suggestion from the agreement between the Y-intercept value and the Ca added to the soil is that if no leaching had taken place, and no Ca had been needed to neutralize soil acidity, and no Ca had been removed by crops, all the Ca added would have precipitated as CaCO_3 . Thus, the formulas proposed by Eaton (1950) for estimating the Na hazards of waters containing HCO_3^- are appropriate if the soil is alkaline (pH near 8), and there is no leaching or crop removal of constituents in the water. With crop removal or increased leaching the formulas overestimate the Na hazard. If the soil is acid the formulas do not apply until the usually alkaline pH values of calcareous soils are attained.

The average CaCO_3 in the soil was approximately 50 per cent of the CaCO_3 equivalent of the total Ca added. The relationship between CaCO_3 in the soil and half the CaCO_3 equivalent of the Ca added for each of the four winter crop treatments is presented in figure 4. There was a significant correlation between the two. When all data were considered seventy-one per cent of the variations in CaCO_3 in the soil was associated with variations in the measured Ca added. A large fraction of the unaccounted-for variation is undoubtedly a result of large differences in leaching percentage between the straw and the mustard treatments where $\text{Ca}(\text{NO}_3)_2$ was added. The leaching with mustard was 5.0 per cent whereas with the straw treat-

TABLE 9

CARBONATE-C CONTENT OF SOIL AND SODIUM ADSORPTION RATIO (SAR)
FOR THE SATURATION EXTRACT OF FIVE DEPTHS OF SOIL FROM
TANKS TREATED WITH CEREAL STRAW OR COVERCROPPED
WITH MUSTARD, VETCH, AND MELILOTUS

Depth	Winter cropping treatments*							
	Straw		Mustard		Vetch		Meliilotus	
	C	SAR	C	SAR	C	SAR	C	SAR
inches	per cent		per cent		per cent		per cent	
0- 6.....	0.0043	1.9	0.0114	1.8	0.0012	2.1	0.0015	1.9
6-12.....	0.0046	2.2	0.0114	2.4	0.0040	2.7	0.0029	2.8
12-24.....	0.0060	2.4	0.0130	3.2	0.0135	3.3	0.0106	2.8
24-36.....	0.0058	4.2	0.0092	5.6	0.0108	6.4	0.0104	6.0
36-48.....	0.0023	4.9	0.0029	6.5	0.0036	6.4	0.0047	8.0

* The data for each winter cropping treatment are averages for three rates of N application. The N application increased the magnitude of the CaCO_3 precipitation but had no effect on the relationships between depth and lime or depth and SAR.

ment it was 7.6 per cent. There may have also been some effect of greater CO_2 production by the mustard crop than by the straw treatment.

Data for the CaCO_3 equivalent of the HCO_3^- added in the irrigation water and the CaCO_3 in the soil as a per cent of the HCO_3^- added are presented in table 8. The average precipitation of HCO_3^- was 39.9, 74.0 and 84.8 per cent, respectively, for 0, 100, and 200 pounds N per acre as $\text{Ca}(\text{NO}_3)_2$. Where N was added there was a greater per cent precipitation of HCO_3^- with mustard than with the two legume crops, and this difference is not related to differences in leaching because the leaching was the same at the 100-pound N rate. These data along with data of figure 4, suggest that the type of crop has an influence on CaCO_3 precipitation exclusive of the effect of the crop on leaching percentage. Perhaps this difference resulted from differences in amount of Ca absorption by the crops.

The index defined by C. A. Bower (1958) was calculated for each lysimeter tank. This index is $\text{pH}_s - \text{pH}_e$ where pH_s is the pH of the saturated soil paste and pH_e is the pH that would be in equilibrium in CaCO_3 at the Ca^{++} and HCO_3^- concentrations in the irrigation water. The pH_e is calculated from the following formula:

$$\text{pH}_e = (\text{pK}_2' - \text{pK}_c') + \text{pCa} + \text{pAlk.}$$

Where pK_2' is the negative logarithm of the second dissociation constant of H_2CO_3 , pK_c' is the negative logarithm of the solubility product constant of $CaCO_3$, and pCa and $pAlk$. are the negative logarithms of the Ca and alkalinity concentrations respectively. The alkalinity is the total alkalinity to the methyl orange end point, expressed as HCO_3^- .

The Ca concentration of the irrigation water was adjusted to take into consideration the Ca added in straw and $Ca(NO_3)_2$ by dividing the total Ca added in the water, fertilizer, and straw, by the total volume of irrigation water applied.

The relations between per cent HCO_3^- precipitation and the modified saturation index for all cropping treatments are presented in figure 5. There

TABLE 10
EXCHANGEABLE Na PERCENTAGE AND pH FOR SOIL IN LYSIMETER
TANKS COVERCROPPED TO VETCH AND TREATED WITH THREE
RATES OF $Ca(NO_3)_2$

Depth, inches	Rate of $Ca(NO_3)_2$, lbs N per acre					
	0		100		200	
	pH	Exch. Na	pH	Exch. Na	pH	Exch. Na
0-6.....	7.9	5.1	7.8	5.3	7.5	5.3
6-12.....	8.0	4.8	8.0	4.5	7.8	4.9
12-24.....	8.2	7.8	8.3	6.8	7.9	4.4
24-36.....	8.4	14.9	8.4	10.5	8.0	8.5
36-48.....	8.1	12.8	7.9	13.0	7.7	10.2

was a significant correlation between the modified saturation index and the percentage of HCO_3^- precipitation; there was also a difference in the crops. The combination of $Ca(NO_3)_2$ with mustard winter covercrop produced a greater per cent precipitation of the HCO_3^- than the two other covercrops or the straw treatments.

Carbonate-C content and sodium adsorption ratio (SAR) of the saturation extract of soil of five depths are presented in table 9. The rate of application of $Ca(NO_3)_2$ (pounds N per acre) had no effect on relations between soil depth and lime content or SAR; thus the data were averaged for each cropping treatment.

With each treatment the maximum precipitation of lime was in soil of the 12- to 24-inch depth. In the case of the straw applications and mustard covercrop treatment, the differences in amounts of lime content of the first 2 feet of soil were not great, whereas in the legume covercrop treatments the first foot of soil contained much less lime than the second and third feet.

In all cases the greatest increase in SAR was at a depth just below that of the maximum precipitation of carbonates. Thus there is a direct cause-and-effect relationship between precipitation of $CaCO_3$ and the SAR of the water that moves on to the lower layers of the soil.

Both the precipitation of $CaCO_3$ and the differential absorption by plants of Ca and Mg relative to Na, influence the SAR of the water in the soil. In

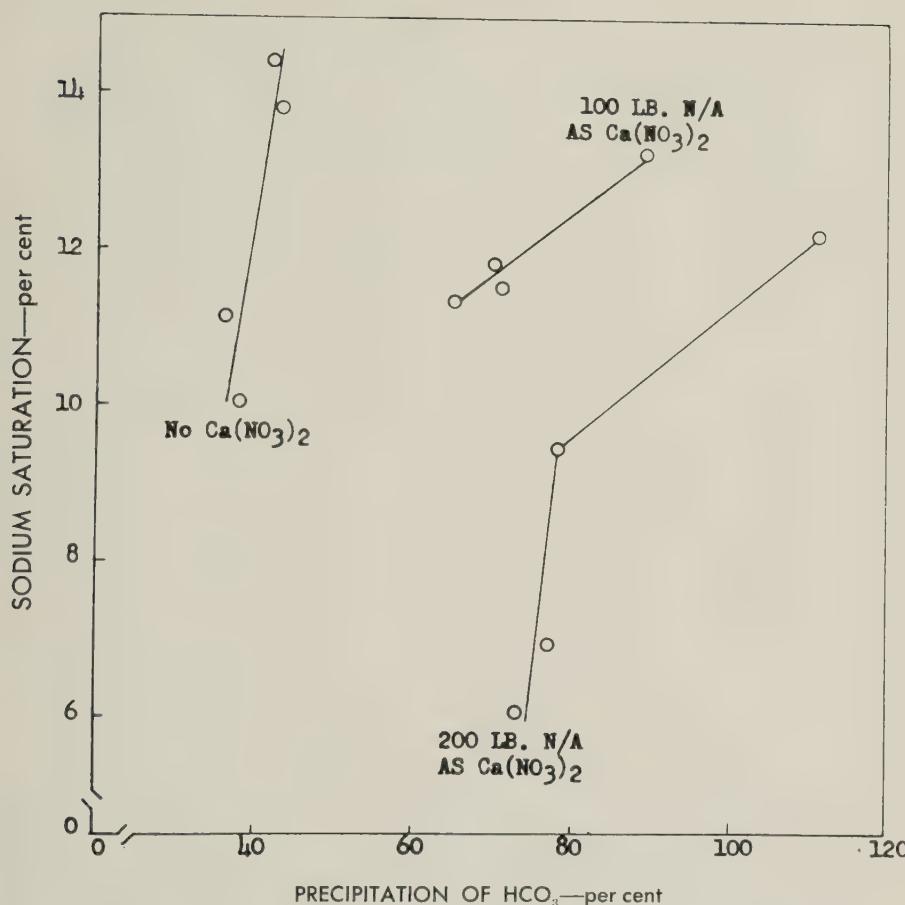


Fig. 6. Relations among Na saturation of the soil of the 24-36-inch depth, precipitation of the HCO_3^- added in the irrigation water and the annual rate of application of $\text{Ca}(\text{NO}_3)_2$ fertilizer.

In this experiment the removal of Na by plants was 8.5% of that added, whereas with Ca and Mg, removal by plants was 14.6 and 48%, respectively. The SAR of the water was 1.16; thus all saturation extracts showed a higher SAR than the water.

Data for pH and per cent exchangeable Na for soils winter-covercropped to vetch at three rates of N are presented in table 10. The data for the third foot of soil at the O rate of N show that the soil at this depth was approaching alkali or sodic characteristics. The $\text{Ca}(\text{NO}_3)_2$ applications had a soil amendment effect in reducing both the pH and the per cent exchangeable Na at the lower depths.

The relations among Na saturation of the 24- to 36-inch depth of soil, precipitation of the HCO_3^- added in the irrigation water, and the rate of application of N as $\text{Ca}(\text{NO}_3)_2$ are presented in figure 6. These data provide

additional evidence that the precipitation of CaCO_3 increased the sodium saturation and also that the $\text{Ca}(\text{NO}_3)_2$ served as a soil amendment in reducing sodium saturation. Within each rate of application of $\text{Ca}(\text{NO}_3)_2$ the Na saturation increased with increase in CaCO_3 precipitation. The overall effect, however, of the $\text{Ca}(\text{NO}_3)_2$ was to reduce Na saturation.

Salts in Drainage Water. Data for the amounts of soluble constituents of the drainage water for the 1951-52 season are presented in table 11. This leaching followed a period of 7 years in which there was no drainage water and thus represents the maximum salt content of the drainage water in the experiment. The solution was mainly a mixture of sulfate salts with about

TABLE 11
ANALYSIS OF DRAINAGE WATER FOR 1951-52 SEASON

Tank number and treatment	Acre-inches	pH	Composition of drainage (me/liter)							
			Ca	Mg	Na	K	$\frac{\text{CO}_3}{\text{HCO}_3^-}$	Cl	SO_4	NO_3
1. Straw.....	1st.....	7.0	24.8	13.7	18.3	0.2	1.0	4.3	50.8	1.0
	2d.....	7.1	20.6	10.7	15.8	0.2	1.8	3.7	42.2	1.4
	3d.....	7.6	13.4	7.1	11.5	0.1	1.8	4.3	26.1	2.2
2. Vetch.....	1st 2/3.....	8.1	20.0	9.3	25.9	0.4	3.2	5.8	40.3	9.9
3. Melilotus.....	1st.....	7.3	23.4	13.1	30.8	0.4	4.9	5.0	56.7	2.7
	2d.....	8.2	19.1	8.8	27.2	0.3	5.3	4.0	46.2	2.6
	3d.....	8.4	14.3	6.5	22.6	0.2	7.5	2.9	34.1	1.9
4. Mustard.....	1st.....	7.7	22.9	10.7	18.7	0.2	4.5	4.6	44.1	0.1
	2d.....	7.6	19.7	9.1	16.8	0.2	5.0	4.7	36.6	0.1
	3d.....	8.2	14.7	6.5	15.4	0.1	5.3	4.4	26.9	0.2
	4th.....	8.2	12.5	5.8	13.7	0.1	5.9	4.0	21.9	<0.0
	5th.....	8.1	11.1	5.3	13.3	0.1	7.4	3.8	19.6	0.1
	6th.....	8.4	8.0	4.1	10.6	0.1	8.0	2.8	14.0	0.1

equal amounts of Na and Ca. The Cl content was low because the crops removed 81 per cent of that added, and the HCO_3^- was low because of precipitation as CaCO_3 . Relative to the composition of the irrigation water the Na and SO_4 ions showed the greatest concentration effect.

Exchangeable Cations in the Soil. The soil as it was put into the tanks had a uniform depth distribution of exchangeable cations. Thus any differences found at the end of the experiment are a result of changes that have resulted from crops, irrigation water, and fertilizer.

The depth distribution of the cation-exchange capacity changed only slightly. The C.E.C. of the surface six inches was 7.1 compared to a value of about 6.2 in the lower depths. This difference is probably a result of some accumulation of organic matter in the surface and loss of organic matter at the lower depths.

The average depth distribution of exchangeable K was 4.6, 3.0, 2.3, 2.2 and 2.1 per cent saturation for soil of the 0-6, 6-12, 12-24, 24-36 and 36-48-inch depths respectively. For the most part, distribution is probably a result of the deposition of K on the surface soil by growth of the winter crops. The only treatment that included additions of K to the soil was application

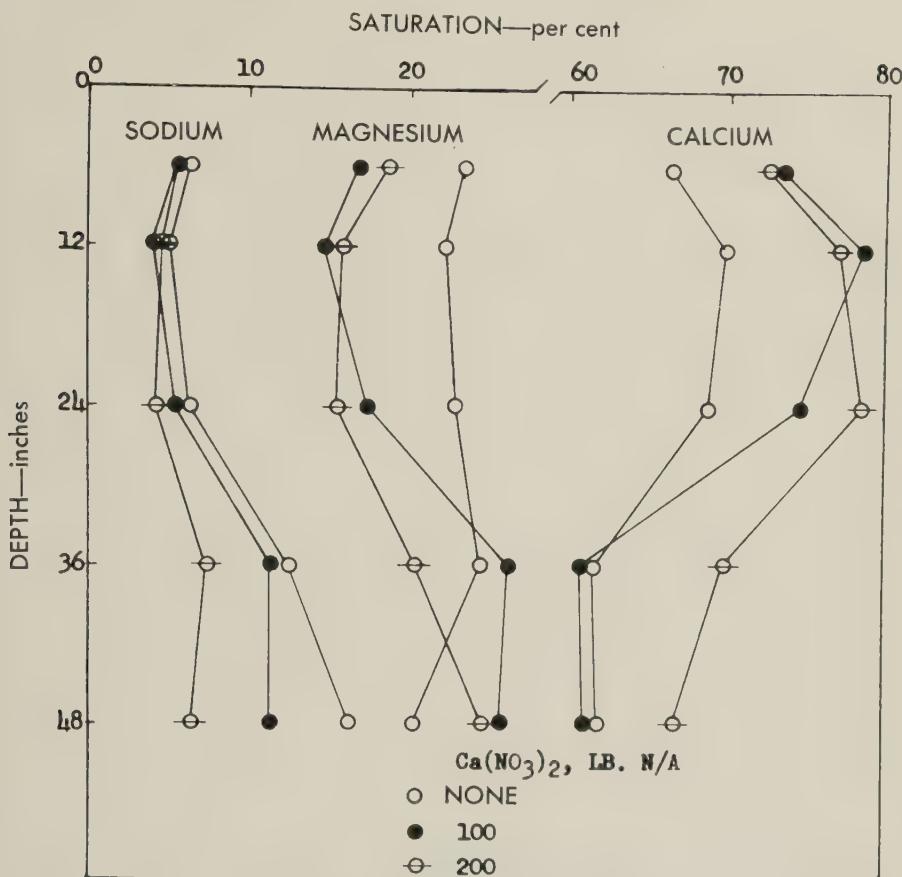


Fig. 7. Relations among saturation of soil with Ca, Mg, and Na depth of soil and rate of application of $\text{Ca}(\text{NO}_3)_2$ fertilizer.

of cereal straw. However, the distribution of exchangeable K was qualitatively the same in all tanks, although the highest K saturation in the surface six inches of soil was in tanks that received cereal straw.

The relations among saturation of the soil with Ca, Mg and Na, depth of soil and rate of application of $\text{Ca}(\text{NO}_3)_2$ are presented in figure 7. The increased Ca saturation of the surface 0 to 24-inch depth of soil that resulted from the application of $\text{Ca}(\text{NO}_3)_2$ was mainly balanced by a decrease in Mg saturation. In the soil at the lower depths the Mg saturation at the intermediate $\text{Ca}(\text{NO}_3)_2$ level increased with a corresponding decrease in Na saturation and, at the highest rate of $\text{Ca}(\text{NO}_3)_2$, Ca increased with a decrease in both Mg and Na.

Under the conditions of the experiment the Ca added in water and in fertilizer was sufficient to prevent Na accumulation in the 0 to 24-inch depth of soil and also sufficient to replace Mg. The replaced Mg moved down and partially prevented Na accumulation in the lower depths. The data suggest

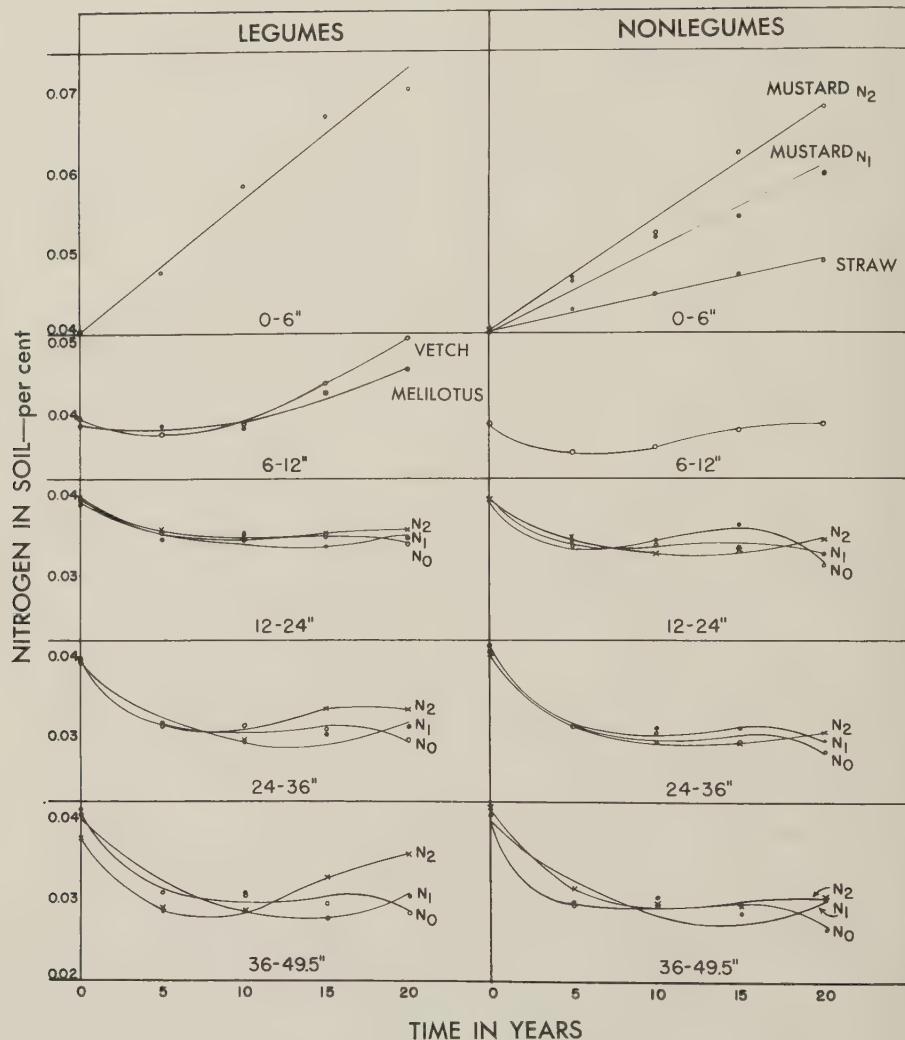


Fig. 8. Relationships between total N in soil at five depths and time for legumes, nonlegumes and three rates of N application.

that a slightly higher leaching percentage would have prevented Na accumulation in the lower depths but would have also greatly increased the Mg loss.

Total Nitrogen and Organic Carbon in the Soil. The relations between total N in the soil, depth of soil and time in years beginning with treatments in 1933 are presented in figure 8. The first seven years of fallow made little or no difference in the total N in the soil. Any nitrate produced must have stayed where it was produced because the depth distribution of total N did not change during the fallow period. To produce the curves shown in figure

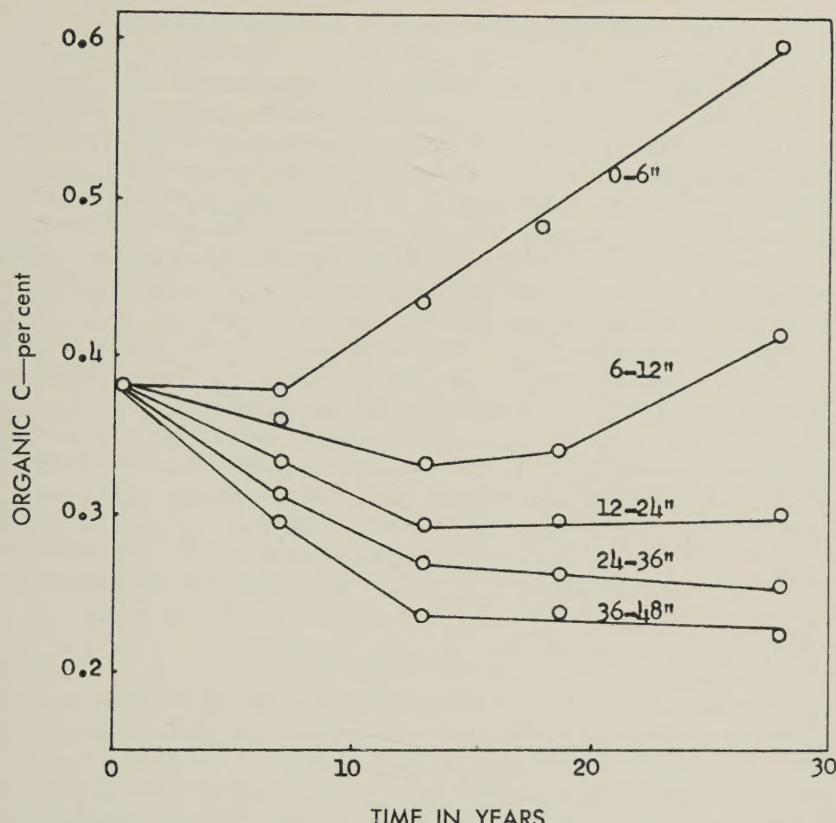


Fig. 9. Relation between organic C in the soil and time beginning when the soil was placed in the lysimeters. The treatment for the tank from which these data were obtained was growth of vetch with no N application.

8 the data were combined until statistically significant differences in regression coefficients were found, and these regression equations were plotted in the figure along with the data. Thus all differences shown in the figure are statistically significant.

The legumes and mustard with added N increased the total N in the surface six inches of soil. In all cases there was a decrease and then an increase in the 6- to 12-inch depth of soil. In the depths below 12 inches there was a decrease with time with an indicated equilibrium attained after 10 years of treatment or 17 years of total time the soil was in the tanks. Small variations in total N in the lower depths during the last 10 years were associated with variations in NO_3^- -N accumulation from $\text{Ca}(\text{NO}_3)_2$ applications.

The relation between organic C in the soil and time beginning when the soil was placed in the tanks is presented in figure 9. The data in figure 9 are for soil treated with vetch winter crop with no N applied. All other tanks were similar, except for very small differences in the amount of

organic C in the soil below 6 inches and some differences in organic C in the 0 to 6-inch depth.

During the first seven years the soil was fallowed with no vegetation allowed to grow. Thus the decrease in organic C during these years is entirely a result of differences in rate of oxidation of organic matter and in no way is related to differences between production and destruction. The most logical explanation for the fact that organic C disappeared faster in the lower horizons is as follows: During the rainy season, when moisture was adequate for mineralization of organic matter, the soil was too cool; when soil became sufficiently warm the rainy season was completed, surface soil was dry, and the moisture increased with increase in depth so that the rate of decomposition of organic matter increased with increase in depth. When cropping started production minus decomposition was greatest in the surface layer and decreased with increase in depth so that the trends started in the first 7 years with a fallow system were continued under the cropping system. The attainment of equilibrium at the lower depths and reversal of the downward trend in the 6- to 12-inch depth coincided with the change of the summer crop from barley to Sudangrass. The depth distribution of organic C in the soil at the end of the experiment was nearly the same as the distribution of organic C in the agricultural soils in the area where the experiment was conducted.

SUMMARY

The data from a 20-year lysimeter investigation with an irrigated soil have been presented and discussed. The following paragraphs summarize the results.

Yields of Crops. Applications of N to winter annual legumes produced small but consistent increases in yields. There were large increases in yields of winter-grown mustard as a result of N applications. The summer crop, which was barley for the first 6 years and the Sudangrass the rest of the time, gave no increased yield from N where a winter legume was grown and turned under and relatively small increases where mustard was grown as a winter crop or where straw was added in the winter.

The growth of vetch and melilotus winter legumes were as effective as mustard as a winter crop plus 135 pounds N per acre in supplying the summer crop with N.

Nitrogen. Nitrogen fixation by the winter legumes was 131, 106, and 77 pounds per acre per year for vetch treated with 0, 100 and 200 pounds N per acre per year respectively. Comparable data for melilotus were 124, 82 and 67 pounds N per acre per year respectively. There were no significant gains or losses of N in the tanks treated with straw or the growth of mustard in combination with N applications.

Phosphorus. The average depletion of P from the soil was 15.9 pounds P per acre per year.

Potassium. The average depletion of K was 181 pounds K per acre per year.

Magnesium. There was a small average loss of Mg from the soil. However within each winter crop or crop residue treatment there was a decrease in

Mg accumulation or an increase in Mg loss with increase in the rate of application of N as $\text{Ca}(\text{NO}_3)_2$.

Sodium. The average Na accumulation was 116 pounds per acre per year, which was 69 per cent of the Na added.

Chloride. The average accumulation of Cl was 3 pounds per acre per year or about 2 per cent of that added. About 81 per cent of the added Cl was removed by the summer crop and about 17 per cent was removed by leaching.

Sulfur. The average S accumulation was 16.8 pounds per acre per year which was 48 per cent of that added.

Calcium. The average Ca accumulation was 62 per cent of that added. Eighty-six per cent of the Ca accumulated was precipitated as CaCO_3 in the soil and 14 per cent was used in neutralizing soil acidity. The CaCO_3 precipitated in the soil was significantly related to leaching percentage, type of crop and to total Ca added. The Ca added as $\text{Ca}(\text{NO}_3)_2$ had a soil amendment effect in reducing the exchangeable Na.

Drainage Water. Because of crop removal of Cl and precipitation of HCO_3^- as CaCO_3 , the drainage water in the 1951-52 season was mainly a solution of SO_4 salts. Sodium and SO_4 showed the greatest concentration relative to the composition of the irrigation water.

Exchangeable Cations in the Soil. The exchangeable K decreased with increase in depth. Applications of Ca as $\text{Ca}(\text{NO}_3)_2$ displaced Mg from the surface layers (0- to 24-inches) and prevented accumulation of Na in the soil of the same depth. Exchangeable Na accumulated in the 24- to 48-inch depth and where $\text{Ca}(\text{NO}_3)_2$ was added exchangeable Mg accumulated in the same depths.

Total Nitrogen and Organic Carbon. Losses of N and organic C were greatest at the lowest depths. The surface soil increased in both N and organic C during the 20 years of cropping but there were no changes during the 7 years of fallow that preceded the cropping period. However, during the fallow period the lower depths lost organic C.

LITERATURE CITED

ALLISON, F. E.
 1955. The enigma of the soil nitrogen balance sheets. *Adv. in Agron.* 7: 213-250.

BOWER, C. A.
 1958. Prediction of the effects of irrigation waters on soils. *Proc. UNESCO Arid Zone Symposium.* Tehran, Iran.

BROADBENT, F. E., and H. D. CHAPMAN
 1950. A lysimeter investigation of gains, losses, and balance of salts and plant nutrients in an irrigated soil. *Soil Sci. Soc. Amer. Proc.* (1949) 14: 261-269.

CHAPMAN, H. D., G. F. LIEBIG, and D. D. RAYNER
 1949. A lysimeter investigation of nitrogen gains and losses under various systems of covercropping and fertilization, and a discussion of error sources. *Hilgardia* 19: 57-128.

EATON, F. M.
 1950. Significance of carbonates in irrigation waters. *Soil Sci.* 69: 123-133.

PRATT, P. F., and R. B. HARDING
 1957. Decreases in exchangeable magnesium in an irrigated soil during 28 years of differential fertilization. *Agron. Jour.* 49: 419-421.

